

# Preparation and Properties of Pure Ammonium DL-Lactate<sup>1</sup>

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Ammonium lactate, which can readily be prepared by fermentation of carbohydrates in the presence of ammonia<sup>2-4</sup> is potentially an important primary fermentation product. Previous studies at this Laboratory have shown that ammonium lactate upon interaction with alcohols produces lactic ester and ammonia in high yields.<sup>5-7</sup> However, comparatively little information about the physical properties of ammonium lactate has been reported,<sup>8-11</sup> only the distillation of ammonium lactate in vacuum<sup>10</sup> and certain properties of aqueous ammonium lactate<sup>11</sup> having been recorded. Pure crystalline ammonium lactate, however, was not used in these investigations, and lactamide was most likely a contaminant.<sup>12</sup> This paper reports the preparation of pure crystalline ammonium lactate and the determination of various properties of this pure salt.

## Experimental

**Preparation of Ammonium Lactate.**—The equivalence point of ammonium lactate was first determined as follows: An approximately 0.1 *N* lactic acid solution was prepared by diluting a high quality 20% lactic acid solution and refluxing for one day to completely remove any polylactic acid. A 25-cc. aliquot of this solution (0.098 *N*) was titrated potentiometrically with freshly standardized ammonium hydroxide (0.102 *N*). The change in pH in the vicinity of the equivalence point was pronounced, considerably more than in the titration of a weaker acid such as acetic acid. The equivalence point for ammonium lactate corresponded to a pH of 6.65.

The 80% edible grade DL-lactic acid of commerce (4 kg.) was diluted to approximately 20% concentration with water (12 kg.) and this diluted solution was heated under a reflux condenser for 24 hours at 85–90°. Thus the polylactic acid, present in concentrated lactic acid solutions, was almost completely hydrolyzed to lactic acid. The equilibrated 20% aqueous lactic acid solution was then neutralized with concentrated ammonium hydroxide to a pH of 7.0. The dilute ammonium lactate solution was concentrated in a steam-heated laboratory-size glass circulating evaporator<sup>13</sup> operated at 30 mm. Because of the explosion hazard<sup>14</sup> resulting from mercury exposed to ammonia, the pressure was initially adjusted to 30 mm.; the manometer then was closed from the system and the pressure periodically checked by momentarily opening the mercury manometer to the system. The solution was evaporated until its temperature reached 70°. The concentrated ammonium lactate

solution was then withdrawn from the evaporator, and the pH, which was approximately 6, was adjusted to 6.7 by addition of concentrated ammonium hydroxide. Analysis of the solution by the formol titration method<sup>15</sup> showed an ammonium lactate content of 84.5%. Analysis of the solution for total nitrogen<sup>16</sup> and for ammonia nitrogen by the magnesium oxide method<sup>17</sup> showed 11.1 and 11.0% nitrogen, respectively; thus the salt was essentially free of lactamide.

**Crystalline Ammonium Lactate.**—To 100 g. of 84.5% aqueous ammonium lactate was added 250 ml. of benzene and the stirred mixture was refluxed for 3.5 hours (pot temp., 79–85°) with continuous removal of water; a water separating trap was employed to separate water from its benzene azeotrope. Benzene was then evaporated in vacuum from the reaction mixture and the resulting sirupy liquid was stored in a refrigerator. Crystals slowly separated over a storage period of approximately one month and these were removed by filtration.

Once crystals were obtained it was more convenient to isolate the solid ammonium lactate as follows: 500 g. of 84.5% ammonium lactate solution was cooled in an ice-bath, after which seeds of crystalline ammonium lactate were added to the cooled solution. On filtration 268 g. (63% of the salt in solution) of crystalline ammonium lactate was collected.

At room temperature the crystalline salt was soluble in water, glycerol and 95% ethyl alcohol; slightly soluble in methanol; and insoluble in absolute ethyl, *n*-propyl, isopropyl and *n*-butyl alcohols, ether, acetone and ethyl acetate. With the exception of isopropyl alcohol, acetone and ether, the solid salt was soluble in these solvents at approximately their boiling temperatures. A saturated solution of ammonium lactate in water at 20°, analyzed by the formol titration method,<sup>15</sup> contained 224.7 g. of salt per 100 g. of water, corresponding to a 69.2% solution.

*n*-Propyl alcohol was found to be the best solvent for recrystallization of ammonium lactate. Two recrystallizations from *n*-propyl alcohol resulted in an anhydrous salt melting at 91–94°.

**Anal.** Calcd. for C<sub>3</sub>H<sub>7</sub>O<sub>2</sub>N: NH<sub>3</sub>, 15.90; lactic acid, 84.10. Found: NH<sub>3</sub>, 15.78; lactic acid, 84.10.

**Physical Properties of Aqueous Ammonium Lactate.**—Solutions of various concentration were prepared by dissolving the pure crystalline salt in distilled water. The refractive index, density and viscosity were determined at 20, 25 and 40° by standard procedures. The results are shown in Table I.

**Distillation of Ammonium Lactate.**—Crystalline ammonium lactate, 51 g., was distilled in an alembic still<sup>18</sup> at 0.2 to 0.4 mm. and 38 g. of a colorless sirupy liquid was collected at 76.5 to 83°. (Care was taken as described above to prevent ammonia from contacting the mercury in the manometer.) In accordance with observations of previous investigators,<sup>10</sup> the distillate appeared to be a complex of equimolar amounts of ammonium lactate and lactic acid, CH<sub>3</sub>CHOHCO<sub>2</sub>NH<sub>4</sub>·CH<sub>3</sub>CHOHCO<sub>2</sub>H. **Anal.** Calcd. for C<sub>6</sub>H<sub>13</sub>O<sub>6</sub>N: N, 7.10; neut. equiv., 197.2. Found: N, 6.85; neut. equiv., 195.8. Formol titration showed an equivalent weight as an ammonium salt of 214 (theoretical value, 197.2).

The distillate was redistilled at various pressures in the range of 0.1 to 10 mm.; the following boiling points were observed: 74° at 0.14 mm., 89.5° at 0.50 mm., 99° at 0.75 mm., 102.5° at 1.00 mm., 130° at 4.20 mm., and 141° at 8.30 mm.

**Preparation of Dibutylammonium Lactate from Ammonium Lactate.**—A mixture of 74% aqueous ammonium lactate (1 mole) and di-*n*-butylamine (1 mole) was refluxed for two hours to remove ammonia. On cooling in the refrigerator, a solid crystallized from the reaction mixture. The

- (1) Article not copyrighted.
- (2) H. C. Jansen, Dutch Patent 57,848 (July 15, 1946).
- (3) L. H. C. Perquin, Dutch Patent 58,545 (Nov. 15, 1946).
- (4) L. L. Kempe, H. O. Halvorson and E. L. Piret, *Ind. Eng. Chem.*, **42**, 1852 (1950).
- (5) E. M. Filachione, E. J. Costello and C. H. Fisher, *THIS JOURNAL*, **73**, 5265 (1951).
- (6) E. M. Filachione and E. J. Costello, *Ind. Eng. Chem.*, **44**, 2189 (1952).
- (7) E. M. Filachione and C. H. Fisher, U. S. Patent 2,565,487 (Aug. 28, 1951).
- (8) B. E. Brown and F. R. Reid, *Am. Fertilizer*, **95**, No. 12, 12 (1941).
- (9) F. Groebe and O. Spengler, German Patent 680,660 (Aug. 17, 1939).
- (10) R. Escalles and H. Koepke, *J. prakt. Chem.*, **87**, 258 (1913).
- (11) A. A. Dietz, E. F. Degering and H. H. Schopmeyer, *Ind. Eng. Chem.*, **33**, 1444 (1941).
- (12) J. Wislicenus, *Ann.*, **133**, 257 (1865).
- (13) D. T. Mitchell, P. Schildneck and J. Dustin, *Ind. Eng. Chem., Anal. Ed.*, **16**, 754 (1944).
- (14) I. I. Sampey, *Chem. Eng. News*, **25**, 2138 (1947).

- (15) A. Ronchese, *J. pharm. chim.*, **25**, 611 (1907); *Analyst*, **32**, 303 (1907).
- (16) C. O. Willits, M. R. Coe and C. L. Ogg, *J. Assoc. Offic. Agr. Chemists*, **32**, 118 (1949).
- (17) Association of Official Agricultural Chemists, "Official and Tentative Methods of Analysis," 6th ed., 2.29, p. 28, Washington, D. C. 1945.
- (18) W. P. Ratchford and C. E. Rehberg, *Anal. Chem.*, **21**, 1417 (1949).
- (19) W. P. Ratchford and C. H. Fisher, *J. Org. Chem.*, **15**, 317 (1950).

TABLE I  
PHYSICAL PROPERTIES OF AQUEOUS AMMONIUM LACTATE

Concn., % by wt.	$n_D^{20}$	$n_D^{25}$	$n_D^{40}$	$d_4^{20}$	$d_4^{25}$	$d_4^{40}$	Viscosity, cps.		
							20°	25°	40°
0.0	1.3330	1.3321			0.9971		1.01	0.8	
5.0	1.3407	1.3400	1.3383	1.0132	1.0155	1.0066	1.18	1.04	0.86
15.0	1.3576	1.3557	1.3540	1.0412	1.0385	1.0346	1.53	1.35	0.97
28.8	1.3786	1.3775	1.3756	1.0810	1.0788	1.0730	2.66	2.17	1.60
46.4	1.4064	1.4050	1.4037	1.1288	1.1249	1.1198	6.28	5.22	3.36
70.0	1.4416	1.4406	1.4379	1.1826	1.1808	1.1729	43.05	32.87	16.35
78.8	1.4543	1.4536	1.4503	1.2006	1.1984	1.1904	160.64	115.0	46.31

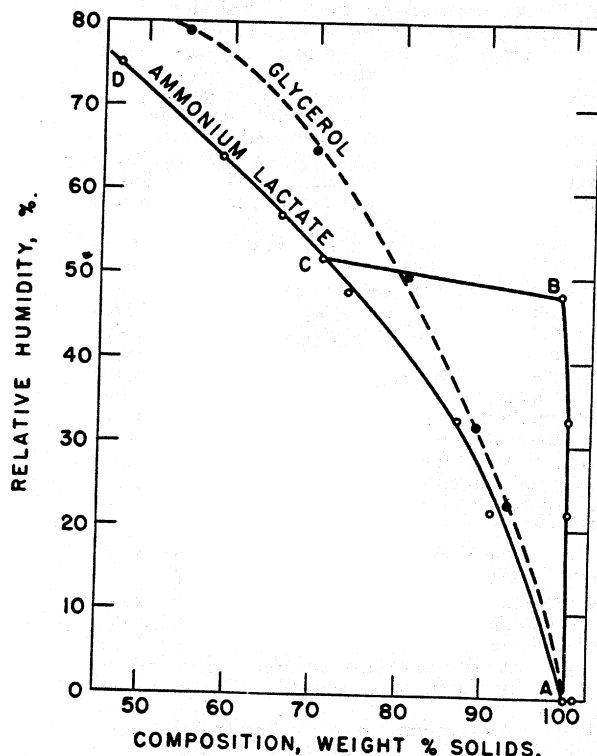


Fig. 1.—Hygroscopicity of ammonium lactate at 25°.

solid was separated and recrystallized from benzene to give 116 g. (53% yield) of dibutylammonium lactate, m.p. 76.5–78°. No attempt was made to recover material in the mother liquors. When the material was mixed with an authentic sample of dibutylammonium lactate<sup>19</sup> the melting point was not depressed.

**Hygroscopic Properties of Ammonium Lactate.**—The apparatus designed by Wink<sup>20</sup> was used in a constant temperature room at  $25 \pm 2^\circ$  to determine the hygroscopicity of ammonium lactate. The procedure was substantially that described for determination of the hygroscopicity of lactamide derivatives.<sup>21</sup> A 2- to 4-g. sample of the salt,

weighed to the nearest 0.2 mg., was distributed on glass wool mats in the dishes of the Wink apparatus. The samples were exposed to atmospheres of various relative humidity and weighed daily until the composition changed less than 0.1% in 24 hours. This composition, usually attained in one to two weeks, was taken as the equilibrium value. Saturated solutions of the following salts, relative humidity at 25° indicated in parentheses, were used to provide constant humidity<sup>20–23</sup>: potassium acetate (22%), magnesium chloride hexahydrate (33%), potassium nitrite (48%), magnesium nitrate hexahydrate (52%), sodium bromide (58%), sodium nitrite (64%) and sodium chloride (75%). Zero humidity was obtained with anhydrous calcium sulfate. The results are summarized in Table II and Fig. 1. For comparison, the curve for glycerol<sup>24</sup> is included in Fig. 1. The absorption curve for ammonium lactate (ABCD, Fig. 1) was obtained by exposing the crystalline ammonium lactate to the various relative humidities. The desorption curve (DCA, Fig. 1) was obtained by transferring equilibrium composition samples to vessels of lower relative humidity. All the equilibrium composition samples corresponding to the points on curve DCA of Fig. 1 were liquid. The liquid samples obtained at relative humidities of zero and 33% crystallized when seeded with solid ammonium lactate. Although other equilibrium compositions were not tested in this manner, presumably all compositions between C and A of curve DCA (Fig. 1) would be super-saturated solutions of ammonium lactate.

TABLE II  
HYGROSCOPICITY OF AMMONIUM LACTATE AT 25°

Relative humidity, %	Equilibrium compn., % $\text{NH}_4$ lactate Absorp. <sup>a</sup>	Desorp. <sup>b</sup>	Relative humidity, %	Equilibrium compn., % $\text{NH}_4$ lactate Absorp. <sup>a</sup>	Desorp. <sup>b</sup>
0	100	101	52	71	..
22	100	91	57	66	..
33	100	87	64	59	59
48	99	74	75	47	..

<sup>a</sup> Crystalline salt exposed to the various relative humidities. <sup>b</sup> Equilibrium compositions, obtained by absorption, transferred to atmospheres of lower relative humidity.

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(22) D. S. Carr and B. L. Harris, *ibid.*, **41**, 2014 (1949).

(23) R. H. Stokes and R. A. Robinson, *ibid.*, **41**, 2013 (1949).

(24) W. C. Griffin, *ibid.*, **37**, 1126 (1945).

(25) One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, United States Department of Agriculture.

(20) W. A. Wink, *Ind. Eng. Chem., Anal. Ed.*, **18**, 251 (1946).

(21) W. P. Ratchford, *Ind. Eng. Chem.*, **42**, 1565 (1950).